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Carbohydrate Polymers as Adhesives

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I. INTRODUCTION

Carbohydrates in the form of polysaccharides are readily available from all plants, the exoskeletons of various marine animals, and some microorganisms. Because up to three-fourth of the dry weight of plants consists of polysaccharides, it is not surprising that many polysaccharides are readily available at low cost. Polysaccharides, especially from plant sources, have served a variety of uses in human history, ranging from basic necessities, such as food, clothing, and fuel, to paper and adhesives.

Three major carbohydrate polymers are readily obtained from biomass and are commercially available. These polysaccharides are cellulose, starch, and gums. The use of each of these types of carbohydrate polymers in and for adhesives is discussed in this chapter.

II. ADHESIVES FROM CELLULOSE

Cellulose is the principal structural material in the cell wall of all plants and is also found in algae, bacteria, and animals (tunicates). Approximately 10^{11} tons of cellulose is formed each year; this puts cellulose among the most important renewable resources in the world [1].

A. Cellulose Structure

Cellulose is a homopolymer of β-D-anhydroglucopyranose monomeric units that are linked via ether linkages between C-1 of one monomeric unit and C-4 of the adjacent monomeric unit (Fig. 1). As illustrated, every other monomeric unit is rotated approximately 180° about the long axis of the cellulose chain when compared to its two neighboring monomeric units. Because of this rotation, cellobiose is usually considered to be the

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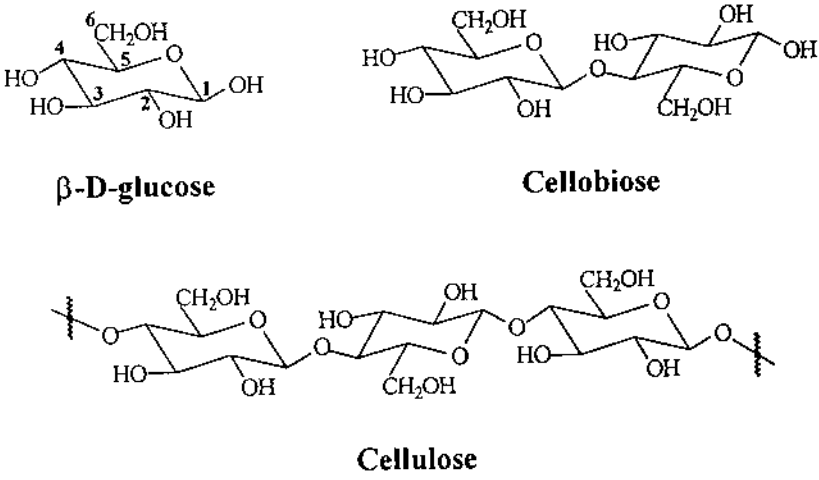

Figure 1 Molecular structures of β-D-glucose, cellobiose, and cellulose. β-D-Glucose is the main building block of cellulose, while cellobiose is the actual repeating unit.

repeat unit of the cellulose polymer. Chain lengths in cellulose can range from 700 to 25,000 glucose units, depending on the source [2]. The two most common sources for cellulose are cotton linters and wood pulp, with approximate chain lengths of 1000–5000 and 500–2100 glucose units, respectively.

As a result of the large number of hydroxyl groups, cellulose molecules readily form hydrogen bonds with other cellulose molecules to give highly crystalline structures. Because the hydrogen bonding between cellulose molecules is not easily disrupted, cellulose does not dissolve in most common solvents. As a consequence, cellulose itself is not useful as an adhesive. Instead, cellulose is converted to various derivatives that can be used in the formulation of adhesives. Both esterification and etherification reactions can be carried out at the hydroxyl groups of cellulose. These cellulose esters and ethers can readily be dissolved into aqueous or organic solvents. Certain derivatives are thermoplastic and thus have been used in plastics and as hot-melt adhesives.

B. Modification of Cellulose

Each glucose unit in a molecule of cellulose has three hydroxyl groups that can be used to derivatize the cellulose by reactions common to all alcohols. It is uncommon, and for some derivatives impossible, to achieve a degree of substitution (DS) of three. Most important derivatives of cellulose have a DS that is somewhat below that value. For a given derivative, the DS must be specified since the properties of the derivative depend almost as much on DS as they do on the substituting agent.

1. *Esters*

Esterification of cellulose to give cellulose trinitrate was discovered by Schönbein in 1846 using a mixture of sulfuric and nitric acids. The resultant compound was so flammable that its first use was as smokeless gunpowder. By the end of the ninteenth century, cellulose nitrates had been prepared with a lower DS, and they could safely be used for other purposes. All cellulose nitrates are prepared by Schönbein's method, in which an

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aqueous slurry of cellulose is reacted with nitric acid in the presence of sulfuric acid (Fig. 2a). The reaction is in equilibrium and thus the removal of water during the reaction forces the reaction to completion [3]. The relative concentrations of the reacting species determine the ultimate DS that can be obtained. Boiling the nitrated product in water removes sulfate groups that can make the cellulose nitrate unstable, and digestion may be the final preparation step if a lower-viscosity material is desired.

The discovery that cellulose esters could be prepared with organic substituents led to the development of cellulose derivatives that had decreased flammability compared to that of cellulose nitrate. The most important organic ester is cellulose acetate. It is prepared by the reaction of acetic anhydride on cellulose in the presence of sulfuric acid. Acetic acid is

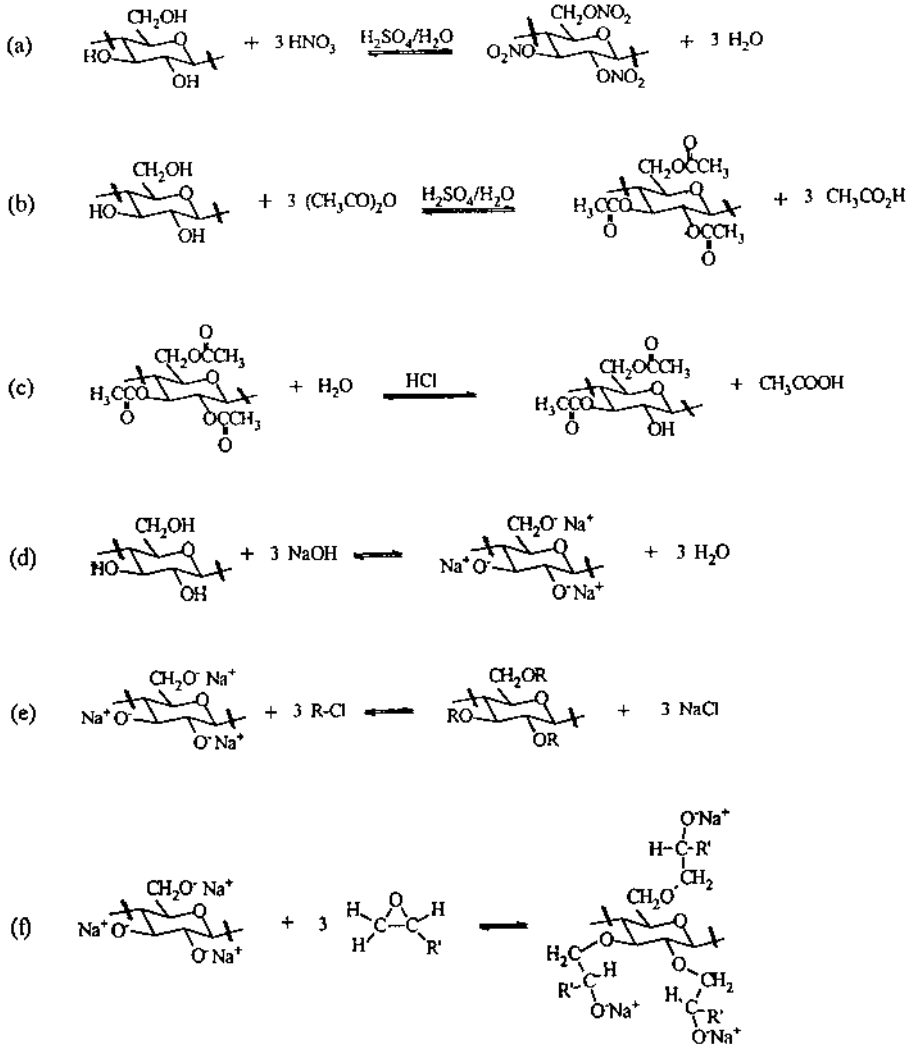

Figure 2 Major reactions of cellulose: (a) nitration by nitric acid; (b) esterification by acetic anhydride; (c) hydrolysis of tertiary cellulose acetate by hydrochloric acid; (d) deprotonation of cellulose, the first step in etherification; (e) etherification of sodium cellulose by an alkyl halide; (f) etherification of sodium cellulose by an epoxide.

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used as the solvent and the reaction is carried out for about 8 h to yield the triester (defined as having a DS greater than 2.75) (Fig. 2b). The derivatives with lower DS values are obtained by the hydrolysis of the triester by hydrochloric acid to yield the desired substitution (Fig. 2c).

Esters of other aliphatic acids are prepared in a similar manner using the appropriate anhydride. Industrially important esters include cellulose propionate, cellulose butyrate, cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). The mixed esters, CAP and CAB, are prepared by using a mixture of anhydrides in the desired ratios, or by reacting cellulose with propionic or butyric acid and acetic anhydride. Both reactions require sulfuric acid as a catalyst.

2. *Ethers*

Cellulose ethers are prepared by replacing the hydrogen on the cellulose hydroxyl groups with an alkyl group. The substitution reaction first involves the removal of the hydrogen by sodium hydroxide to make sodium cellulose (Fig. 2d). The sodium cellulose is then reacted with the appropriate alkyl halide or epoxide. Reaction with an alkyl halide yields the cellulose ether plus sodium halide (Fig. 2e). The epoxide reaction involves opening the epoxide ring (Fig. 2f), yielding a hydroxyl group on the substituent, which is deprotonated in the strongly basic reaction medium. Cellulose ethers that have been used as adhesives include methyl, ethyl, carboxymethyl, hydroxyethyl, and benzyl cellulose.

Methyl cellulose and ethyl cellulose are prepared using methyl chloride and ethyl chloride, respectively, as the alkyl source. Carboxymethyl cellulose (CMC) is the most important ether prepared from cellulose. It is commonly available as its sodium salt, which is prepared in an alcoholic solvent using either chloroacetic acid or sodium chloroacetic acid as the substituting agent. Hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPC) are both prepared using epoxides: ethylene oxide for HEC and propylene oxide for HPC. The reaction is carried out in a water-miscible solvent, such as the lower alcohols. Because the hydroxyethyl and hydroxypropyl substituents have alcohol groups, further reaction can occur at these groups. Therefore, it is possible to get more than three substituents per anhydroglucose unit. For this reason, a quantity called molar substitution (MS) is defined to be the average number of hydroxyethyl or hydroxypropyl groups per ring, including both those attached directly to the ring and those attached to the ether substituent.

C. Properties and Uses

Adhesives derived from cellulose are used in a wide variety of applications that require an economical means for bonding porous substrates. Specific uses and formulations of various cellulose ester and ether adhesives are discussed in the following sections.

1. *Cellulose Nitrate*

Cellulose nitrates with DS values of 1.8–2.3 are used in plastics, lacquers, coatings, and adhesives. The most common use as an adhesive is as general-purpose household cement, in which the nitrate and a plasticizer are dissolved in a mixed ketone–ester organic solvent. Upon application to the substrate, the solution rapidly loses solvent to form tough, moisture-resistant, clear films. These thermoplastic films are prone to discoloration upon exposure to sunlight, and, as might be expected, are very flammable.

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2. *Cellulose Acetate*

Cellulose acetate is the most important ester produced from cellulose; however, its use in adhesives is limited. Both the triacetate (DS greater than 2.75) and secondary acetate (DS of 2.4–2.6) are used industrially in plastics and textiles. The triacetate is soluble in mixtures of organic solvents, and the secondary acetate is soluble in acetone. Cellulose acetate is more heat resistant than cellulose nitrate but is less water resistant and tends to become brittle with age.

3. *Cellulose Acetate Butyrate*

Use of the mixed ether cellulose acetate butyrate helps to overcome some difficulties associated with using cellulose acetate as an adhesive. CAB is soluble in a greater range of organic solvents than is the pure acetate, and it is more compatible with common plasticizers. It can be applied either as a hot-melt adhesive or in a solvent solution. Because CAB is grease resistant, it has been used in paper sizing and coating to make the paper more resistant to staining.

4. *Methyl Cellulose*

Methyl cellulose with a low DS (0.4–0.6) is soluble in dilute aqueous sodium hydroxide. As substitution is increased, the methyl cellulose becomes soluble in water (DS 1.3–2.6), then in organic solvents (DS 2.4–2.6). The most commonly used derivatives have a DS of 1.2–2.0. which results in cold-water solubility and solution stability for pH 2–12. Upon drying, solutions of methyl cellulose give clear, odorless, tasteless films that are resistant to oils and organic solvents. Methyl cellulose is used for paper coating and sizing to impart grease resistance, in ceramics as a binder, as a nonstaining paste for wallpaper, and in adhesives for leather drying. The last application takes advantage of the fact that upon heating, methyl cellulose thickens reversibly. Thus hides that are attached to the platen during the drying process are easily removed when dry. Table 1 shows a formulation for a leather adhesive [4].

5. *Ethyl Cellulose*

In contrast to methyl cellulose, ethyl cellulose is commonly prepared in its organic soluble state with a DS of 2.3–2.6. Films of ethyl cellulose are thermoplastic, and they resist alkali and salts. Because of their organic solubility, the films tend to swell very little in the presence of water. The resistance of ethyl cellulose to chemical degradation has led to its use in films, lacquers, and adhesives. In adhesives, ethyl cellulose may either be applied in a solvent or as a hot-melt.

Table 1 Formulation of Leather Adhesive with Methyl Cellulose

Component	Amount (part)
Methyl cellulose (4 Pa s)	2.0
Plasticizer	0.2
Casein	0.3
Water	97.5

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6. *Carboxymethyl Cellulose*

Carboxymethyl cellulose, generally as its sodium salt, is the most widely used cellulose ether. CMC is water soluble with a DS of 0.4–1.2 in common applications. It was originally used as a replacement for natural gums in adhesives, but it has since developed many uses of its own. Sodium carboxymethyl cellulose is readily water soluble because of its ionic nature; its largest use is in laundry detergents, where it helps to suspend soil particles during washing. This resistance to greases and soil has made CMC useful in fabric sizing as a soil repellant. Because CMC is completely nontoxic, it is used in many food applications, where its affinity for water prevents drying of the product. Although it is generally no longer used as an adhesive, per se, it is still used in adhesives as a thickener.

7. *Hydroxyethyl Cellulose*

Hydroxyethyl cellulose with an MS value greater than 1.6 is soluble in hot or cold water; with an MS value of 2.3–2.6, it is soluble in organic solvents. HEC forms oil- and grease-resistant films that retain clarity over time. It is used as an adhesive in billboards, corrugated board, plywood, and wallpaper, and as a sizing and binding agent in paper products. Although not approved for direct use in food, HEC is used as an adhesive in packaging materials for foodstuffs.

III. ADHESIVES FROM STARCH

Starch is produced by plants as a way to store the chemical energy that they produce during photosynthesis. Starch is found primarily in the seeds, fruits, tubers, and stem pith of plants, most notably corn, wheat, rice, sago, and potatoes. In 1985 alone, more than 1.6 billion kilograms of starch was used in applications involving bonding of materials [5]. Clearly, this makes starch a very important adhesive material.

A. Starch Structure

Like cellulose, starch is a naturally occurring polymer of glucose. It differs from cellulose in two significant aspects: the glucose rings are in the α-D configuration rather than the β-D configuration, and starch can be differentiated into two types of polymers. One polymer, amylose consists of α-D-anhydroglucopyranose monomeric units combined linearly through 1–4 linkages with little or no branching. The other polymer, amylopectin, is linked through 1–4 linkages but also has branches that form at the primary alcohol group on C-6 (Fig. 3). Careful analyses of various starches have shown that there is also an intermediate fraction that is thought to be an infrequently branched amylopectin [6].

The amount of amylose and amylopectin in a starch depends on the source of the starch. Most starches contain 20 to 30% by weight of amylose, although certain hybrids can contain more than 80% amylose. The most commonly available industrial starches are waxy cornstarch, regular cornstarch, high-amylose cornstarch type V, and high-amylose cornstarch type VII, with amylose concentrations of 0, 28, 55, and 70%, respectively [7].

Starch alone suspended in cold water is essentially unable to act as an adhesive because the starch is so tightly bound in granules. The granules consist of crystalline regions where straight-chain molecules and straight sections of branched molecules are aligned. The crystallite regions are linked together by more amorphous areas where the molecules are not aligned. Within the starch granule, the molecules and crystallites are

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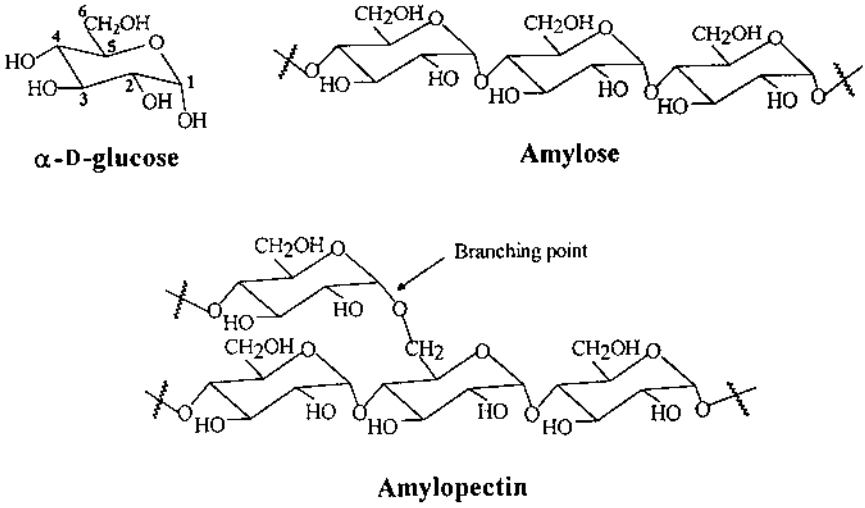

Figure 3 Molecular structures of α-D-glucose and the two major molecules that make up starch, amylose, and amylopectin.

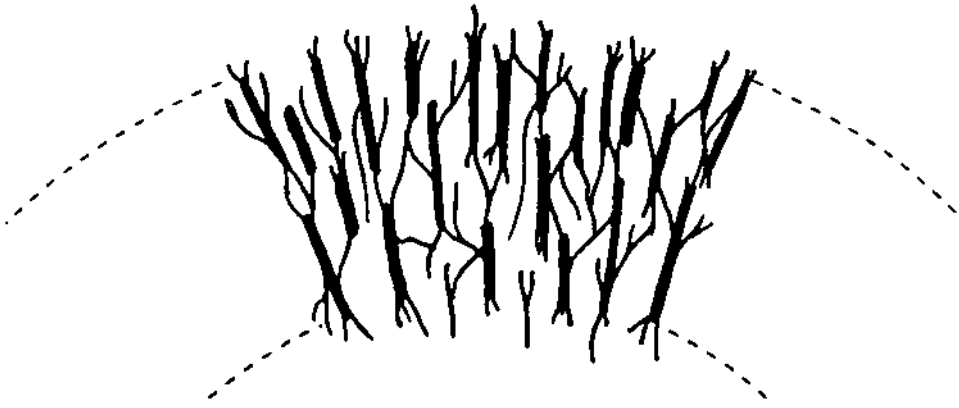

Figure 4 Outer surface of starch granule showing radial arrangement of crystallites. Crystallites are shown as thicker lines. [Adapted from K. H. Meyer, *Adv. Colloid Sci. 1*: 168–169 (1942).]

arranged radially in concentric layers (Fig. 4). It is these granules that must be opened to obtain adhesive bonding.

B. Modification of Starch

Starch must be modified before it can be used as an adhesive. Methods for opening the starch granules include heating, alkali treatment, acid treatment, and oxidation.

1. *Heat Treatment*

The simplest method of breaking up starch granules is well known to the cook. To thicken a sauce, cornstarch must be heated. During the heating process, the starch granules first

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swell and then burst with a coincident thickening of the suspension. The temperature at which this thickening occurs is called the gelation temperature. For starches in pure water, gelation occurs between 57 and 72°C [8]. Observation of gelled starch under a polarizing microscope indicates that the crystallinity of the starch granule is lost during the gelling process. However, the starch is not truly in solution but rather in a colloidal suspension. Suspensions of amylose and high-amylose starches have a tendency to harden and become solid upon cooling. This process is called retrogradation or setback and is a result of the tendency of linear molecules to align with one another. This aligning effect also means that at the same solids content, suspensions with a higher ratio of amylose to amylopectin have a higher viscosity.

2. *Alkali Treatment*

The gelation temperature can be lowered by the addition of sodium hydroxide to a starch suspension. If sufficient alkali is added, the starch can be induced to gel at room temperature.

3. *Acid Treatment (Thin-Boiling Starches)*

Acid modification of starch is achieved by heating the starch to 49–54°C with small amounts of aqueous mineral acid, followed by neutralization with base. The acid acts mainly on the amorphous regions of the starch granules, leaving the x-ray and birefringence patterns of the crystalline regions essentially unchanged. Dried acid-modified starch appears very similar to its unmodified counterpart; however, upon heating a suspension to the gelation temperature, the differences become obvious. The acid modified starch tends to give a much thinner solution at the same solids content when compared to unmodified starch. This makes the modified starch useful in applications that require a higher solids content.

4. *Oxidation*

Oxidized starch is commonly obtained by aqueous alkaline hypochlorite treatment. A starch suspension at pH 8–10 is treated with hypochlorite (5–10% Cl based on starch) for long enough to produce the desired viscosity. Acid is liberated during the reaction, so base must be added to maintain the pH for optimum reactivity. The resultant starch contains a mixture of carboxyl and carbonyl oxygens. Some shortening of chain length is observed during the reaction, but as in acid modification, there appears to be little change in the crystalline region of the starch. Dried oxidized starch is generally whiter than unmodified starch, since the oxidation and subsequent rinsing tend to remove impurities that may be present in native starch. Oxidized starches behave similarly to the acid-modified starches upon gelling. However, the oxidized starches have greater tack and adhesive character, and thus they are used more frequently in adhesive preparations.

C. Dextrins

Dextrins are the product of dry-roasting starch in the presence of an acid catalyst. Although potato, tapioca, and sago starches are the easiest to convert to dextrins, the low cost and ready availability of cornstarch, make it the most commonly used starch. Dextrins are generally divided into three categories: white dextrins, canary or yellow

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dextrins, and British gums. Their differences are determined by the roasting time and temperature and the amount of catalyst used.

1. *White Dextrins*

White dextrins are produced at low temperatures (120–130°C) and roasting times (3–7 h) in the presence of a high concentration of catalyst. The primary reaction that occurs during the formation of white dextrin is hydrolysis of the starch molecules [9]. This reaction initially acts at the 1–6 linkages, and continues with the 1–4 linkages as the concentration of 1–6 linkages decreases. Eventually, repolymerization occurs, which yields small, highly branched dextrins. Very little repolymerization occurs in white dextrins, resulting in a white or buff powder with a degree of polymerization of approximately 20. The solubility of the white dextrins can range from 1 to 95% in water, with the lower-solubility grades resembling starch in their characteristics. The higher-solubility grades are more similar to the lower-conversion yellow dextrins. The small amount of repolymerization in the white dextrins makes the suspensions susceptible to retrogradation, and thus the suspensions must be used soon after preparation.

2. *Yellow Dextrins*

Yellow dextrins are prepared at higher temperatures (135–160°C) and longer roasting times (8–14 h) in the presence of less acid catalyst than are the white dextrins. These conditions promote further repolymerization, yielding a yellow or tan powder with a degree of polymerization between 20 and 50. The yellow dextrins are, for the most part, water soluble; less than 1 part water to 1 part dextrin is required for a working suspension. Yellow dextrin suspensions exhibit good viscosity stability, so retrogradation is less of a problem.

3. *British Gums*

In British gums, the repolymerization reaction is allowed to proceed to the greatest extent. Dry roasting is carried out for 10–24 h at temperatures between 150 and 180°C, and a very small amount of acid catalyst is used. These dextrins tend to be the darkest in color, which ranges from yellow to dark brown. As with the white dextrins, the British gums exhibit a wide range of solubilities in water depending on the exact reaction conditions used. However, the British gums are not prone to retrogradation, and they tend to give a more viscous suspension at the same concentration.

D. Additives and Formulation Variables

The formulation of starch and dextrin adhesives can be viewed more as an art than the result of rigorous scientific study. Not surprisingly, the purpose for which the adhesive is to be used and the method by which it will be applied greatly determine the properties needed in the resin. Factors that must be controlled include viscosity, solids content, stability, tack, slip, substrate penetration, drying rate, flexibility, water and microbial resistance, and cost. Some of these are determined by the type of starch or modification, while others require the addition of an additive to give the adhesive the desired properties. In the sections below we discuss some of the most common additives that are used with starch-derived adhesives.

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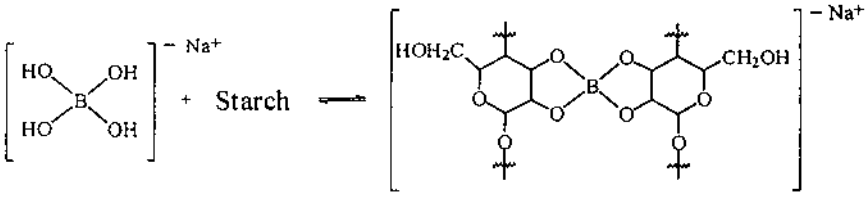

Figure 5 Complexation of starch molecules by the borax in basic solution.

1. *Borax*

Borax (sodium tetraborate) in the presence of small amounts of sodium hydroxide is the most widely used additive to starch-based adhesives. It is commonly used in dextrin adhesives, where it increases the viscosity and acts as a tackifier and viscosity stabilizer. These effects are particularly important in machine application of adhesive to substrate. When used in adhesives, borax is often added in amounts up to 10% based on dry starch before the starch is cooked. Enough sodium hydroxide is added to convert the borax to sodium metaborate, which is the active boron species in thickening. The metaborate is able to hook two starch molecules together, forming a complex (Fig. 5) [10]. If additional sodium hydroxide is added, the complex will dissociate; the viscosity of the suspension will begin to decrease with increasing sodium hydroxide [11].

2. *Plasticizers*

Plasticizers are used to control brittleness of the glue line and to regulate the speed of drying. Commonly used plasticizers act in one of three ways: by forming a solid solution with the dried adhesive, by controlling the moisture in the film, and by lubricating the layers within the dried adhesive. Plasticizers that form a solid solution, such as urea, sodium nitrate, salicylic acid, and formaldehyde, tend to decrease the viscosity of the adhesive preparation. Urea is the most commonly used of these additives, and it may be added at a level of 1–10% based on dry starch. Hygroscopic plasticizers such as glycerol and ethylene glycol are commonly used to decrease the drying rate of the film and ensure that the film does not become brittle. Soaps, polyglycols, and sulfonated oil derivatives are used in small amounts as lubricating adhesives to impart permanent flexibility to the glue line, since they are not affected by changes in humidity.

3. *Additives to Increase Water Resistance*

Starch-based adhesives used in any application that requires water resistance must contain additives that resist water. Commonly used additives of this type are urea–formaldehyde, melamine–formaldehyde, and resorcinol–formaldehyde precondensates, poly(vinyl alcohol), and poly(vinyl acetate). The greatest water resistance is imparted by the formaldehyde-based precondensates; poly(vinyl alcohol) and poly(vinyl acetate) are used for adhesives that are resistant to cold water but can dissolve in hot water.

4. *Viscosity Stabilizers*

As mentioned previously, one problem encountered in starch-based adhesives is retrogradation. Colloid stabilizers such as soaps and sodium chloride are used to retard this tendency. Borax, sodium hydroxide, and several common plasticizers also perform this

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function to some extent, so viscosity stabilizers may not be necessary if these additives are used for other purposes.

5. *Fillers*

Fillers, in amounts of 5 to 50%, are used to control the penetration of the adhesive into the substrate and to control the setting of the glue. Mineral fillers such as clay and bentonite are commonly used.

6. *Other Additives*

Other additives that may be found in starch-based adhesives include preservatives to retard microbial growth, bleaches to remove colored impurities and prevent discoloration of the glue over time, defoamers to prevent foaming during processing, and organic solvents to enhance bonding to waxed surfaces. The most commonly used preservative is formaldehyde, and common bleaches include sodium bisulfite, hydrogen and sodium peroxide, and sodium perborate. Defoaming agents and solvents to be used in starch adhesives must be matched to the type and use of the adhesive, with special attention to compatibility and toxicity of the components.

E. Applications

The majority of starch-derived adhesives are used in the paper and textile industries as binders and sizing materials. However, the discussion in this chapter is limited to glues and pastes, since paper and textile uses have been covered thoroughly elsewhere [12]. This section provides an overview of severa1 gluing applications, with specia1 attention to the properties required of the glue in each case.

1. *Corrugating Adhesives*

Corrugated board is produced by the adhesion of a fluted layer of paper to a flat layer. A two-phase starch adhesive is commonly used to join the two layers. The liquid phase, a gelled mixture of starch and sodium hydroxide in water, is called the carrier. The solid phase of ungelled starch and borax is suspended in the carrier phase. The mixture is applied to a warm fluted sheet, which is then placed into contact with a hot flat sheet. The ungelled starch gels from the heat of the sheets. Table 2 shows a recipe for a typical corrugating adhesive [13].

2. *Bag Manufacture*

Three types of adhesives are used in the manufacture of paper bags and sacks: side-seam adhesive, bottom paste, and cross paste. During production of a single-layer bag, the paper is first formed into a long tube held together by side-seam adhesive. To be compatible with machinery used in this process, the adhesive needs a viscosity in the range 2–4 Pa s with a solids content of 20–22%. Generally, the side-seam adhesive is made using high-soluble white dextrin or acid-modified starch, so the viscosity of the suspension remains low. Bottom paste adhesive is used to close the bottoms of the paper bags; it is much more viscous and has greater tack than side-seam adhesive. The high tack is necessary to keep the bags from opening after they have been formed. Bottom paste adhesives are usually composed of white dextrins or starch; viscosity may be as high as 140 Pa s at 25°C. Cross paste adhesive is used only for the manufacture of multiwall bags. It is similar

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to side-seam adhesive, with the added requirement that it must not bleed through the paper to other layers. This is achieved by the addition of mineral fillers or poly(vinyl acetate). Water resistance of bag adhesives can be improved by the addition of urea–formaldehyde or poly(vinyl alcohol). Typical formulations for these adhesives are listed in Table 3.

Table 2 Recipe for Corrugating Adhesive

Starch adhesive phase	Amount (part)
Liquid (carrier)	
Water	11.9
Starch	3.4
40% Aqueous NaOH	2.0
Cook at 71°C for 15 min	—
Cold water	8.5
Solid (suspension)	
Water	56.6
Borax decahydrate	0.54
Stir to dissolve	—
Starch	16.9
Stir to disperse	—
Add carrier solution	—

Table 3 Typical Formulations for Paper Bag Adhesives

Adhesive and component or process	Amount (part)
Side-seam adhesive	
Water	49.7
White dextrin (94% soluble)	39.7
White dextrin (13% to 15% soluble)	5.0
Borax decahydrate	4.0
Preservative	0.01
Antifoam agent	0.03
Cook to 85°C for 20 to 30 min	—
Cool to room temperature	—
50% Aqueous NaOH	1.2
Bottom paste	
Water	76.7
Starch	19.2
Borax decahydrate	3.1
Preservative	0.2
Soap	0.8
Cook to 93°C for 20 to 30 min	—
Adjust solids to 30%	—

Source: Ref. 14, Chap. 26, p. 14.

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3. *Laminating Adhesives*

Laminates prepared from paper or paperboard may be bonded with carbohydrate adhesives. The properties of the adhesive used with each will differ greatly depending on the surface of the material and the equipment to be used for laminating. However, all laminating adhesives should exhibit high tack, low penetration into the substrate, and noncurling behavior. White dextrin is often used at about 20% of the total adhesive; a typical formulation is given in Table 4.

4. *Carton Sealing*

Cartons from corrugated board are most often sealed with liquid glues or hot-melt adhesives. However, dextrin adhesives are still used as a result of their low cost and ready availability. Adhesives for sealing cartons must have low and stable viscosity, be able to form strong bonds, and set up quickly. If staining of the carton is not a concern, sodium hydroxide may be added to increase adhesion. A formulation for a white dextrin adhesive is given in Table 5.

Table 4 Typical Formulation for a Laminating Adhesive

Component or process	Amount (part)
Water	54.6
White dextrin (high soluble)	20.2
Clay	13.5
Urea	6.7
Borax decahydrate	5.0
Cook to gel	—

Source: Ref. 14, Chap. 26, p. 4.

Table 5 Formulation of Adhesive for Sealing Cartons

Component or process	Amount (part)
Water	110
White dextrin	80
Preservative	2
Borax	12
Antifoam agent	0.125
Cook at 85°C for 20 min	—
Cool to 50°C	—
Water	10
50% NaOH	0.12

Source: Ref. 14, Chap. 26, p. 4.

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Table 6 Formulations for Remoistening Adhesives

Adhesive and component or process	Amount (part)
Envelope adhesive	
Yellow dextrin (95% soluble)	65.7
Water	32.9
Tributyl phosphate	0.2
Heat to 88°C for 30 min	—
Cool to 60°C	—
Corn syrup	1.1
Gummed tape adhesive	
Water	50
Waxy starch (acid-modified)	44
Urea	6

Source: Refs. 15 and 16.

5. *Remoistening Adhesives*

Adhesives for remoistening applications such as tapes, stamps, labels, and envelope flaps must be capable of rewetting. Such adhesives should also be glossy, noncurling, and nonblocking under humid conditions. This requires that the formulation contain acid-modified starch or high-soluble white and yellow dextrins to allow a high solids content. A plasticizer is added to prevent brittleness in the final film. In tape and stamps, the paper with adhesive has traditionally been run over a bar to produce microcracks in the adhesive layer, thus rendering it noncurling. A similar effect has been achieved by solvent deposition of the adhesive. In this process, a cold-water-soluble dextrin is suspended in an organic solvent, where it is insoluble. When this suspension is applied to paper and dries, it leaves behind a layer of discrete dextrin particles, which will not curl. Formulations for two remoistening adhesives are given in Table 6.

IV. ADHESIVES FROM NATURAL GUMS

Gums are hydrophobic or hydrophilic polysaccharides derived from plants or microorganisms that upon dispersing in either hot or cold water produce viscous mixtures or solutions. Natural gums include plant exudates (gum arabic, gum ghatti, gum karaya, gum tragacanth), seed gums (guar gum, locust bean gum, tamarind), plant extracts (arabinogalactan from larch; agar, algin, funoran from seaweed), and the extracellular microbial polysaccharides (xanthan gum, dextran). Gums are used for many industrial purposes, as shown in Table 7. In recent years, synthetic polymers and microbially produced gums increasingly have replaced plant-derived gums.

Historically, several adhesives have been derived from natural carbohydrate polymers. In a few cases, such polymers have been utilized because of their own particular adhesive properties. However, natural carbohydrate polymers are usually used as modifiers for more costly synthetic resins, especially as thickeners, colloidal stabilizers, and flow controllers. Adhesive uses for natural gums include pressure-sensitive tape, denture adhesives, pharmaceutical tablet binders, household products, and label pastes [17].

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Table 7 Applications for Natural Gums

Product	Amount (%)
Detergents, laundry products	16
Textiles	14
Adhesives	12
Paper	10
Paint	9
Food	8
Pharmaceuticals, cosmetics	7
Other	24

V. CONCLUSIONS

Carbohydrates, in the form of polymers such as cellulose, starch, and natural gums, are available in large quantities, especially from plant sources. Each of these has potential for utilization as adhesives and in adhesive formulations. This has been true historically and will be increasingly true in the future as petroleum-derived polymeric materials become scarce and their prices rise. However, because the bonds formed by carbohydrate polymer adhesives are generally sensitive to water, future applications of these adhesives will increasingly depend on modifying the natural polymer to give components that can undergo further cross-linking to form water-insensitive bonds.

REFERENCES

1. V. P. Karlivan, in *CHEMRAWN I*: *Future Sources of Organic Raw Materials* (L.E. St.-Pierre and G.R. Brown, eds.), Pergamon Press, Elmsford, NY, 1980.
2. D. N. -S. Hon, in *Adhesives from Renewable Resources*, ACS Symposium Series 385 (R.W. Hemingway and A.H. Conner, eds.), American Chemical Society, Washington, DC, 1989, p. 291.
3. L. C. Wadworth, and D. Daponte, in *Cellulose Chemistry and Its Applications* (T.P. Nevell, and S.H. Zeronian, eds.), Ellis Horwood, Chichester, UK, England, 1985, p. 349.
4. W. D. Paist, in *Handbook of Adhesives*, 2nd edition, (I. Skeist, ed.), Van Nostrand Reinhold, New York, 1977, pp. 212–221.
5. H. M. Kennedy, in *Adhesives from Renewable Resources*, ACS Symposium Series 385 (R.W. Hemingway, and A.H. Conner, eds.), American Chemical Society, Washington, DC, 1989.
6. R. L. Whistler, and W. M. Doane, *Cereal Chemistry 38*: 251 (1961).
7. L. Kruger, and N. Lacourse, in *Handbook of Adhesives*, 3rd edition, (I. Skeist, ed.), Van Nostrand Reinhold, New York, 1990, pp. 153–166.
8. J. Delmonte, *Technology of Adhesives*, Reinhold, New York, 1947, pp. 277–302.
9. F. Wood, in *Recent Advances in the Chemistry of Starch and Cellulose* (J. Honeyman, ed.), Interscience, New York, 1959, pp. 285–306.
10. F. A. Cotton, and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1980, p. 298.
11. J. A. Radley, in *Industrial Uses of Starch and Its Derivatives* (J. A. Radley, ed.), Applied Science, London, 1976, p. 37.
12. A. H. Zijderveld, and P. G. Stoutjesdijk, in *Recent Advances in the Chemistry and Starch of Cellulose* (J. Honeyman, ed.), Interscience, New York, 1959, pp. 199–228; M. J. Mentzer, in *Starch*: *Chemistry and Technology* (R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds.),

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Academic Press, New York, 1984, pp. 543–574; Starch and starch products in paper coating, *Tappi Monograph 17*, Technical Association of the Pulp and Paper Industry, New York, 1957.
13. W. O. Kroeschell, ed., *Preparation of Corrugating Adhesives*, Tappi Press, Atlanta, GA, 1977, pp. 19–20.
14. A. Blair, in *Handbook of Adhesive Bonding* (C. V. Cagle, ed.), McGraw-Hill, New York, 1973.
15. H. M. Kennedy, and A. C. Fischer, Jr., in *Starch*: *Chemistry and Technology* (R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds.), Academic Press, New York, 1984.
16. J. Lichman, in *Cellulose Chemistry and Its Applications* (T. P. Nevell, and S. H. Zeronian, eds.), Ellis Horwood, Chester, UK England, 1985, pp. 679–691.
17. A. H. Conner, in *Adhesives from Renewable Resources*, ACS Symposium Series 385 (R. W. Hemingway, and A. H. Conner, eds.), American Chemical Society, Washington, DC, 1989.

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